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ADSORPTION AND DESORPTION OF DINITROTOLUENE
ON ACTIVATED CARBON

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Final Report to the U. S. Army
Toxic and Hazardous Materials Agency

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Abstract

The adsorption and solvent extraction of aqueous 2,4-dinitro-toluene (DNT) were evaluated with two commercial activated carbons. Both carbons proved to be excellent adsorbents for aqueous DNT. The solvents tested for extracting the adsorbed DNT were water, acetone, and methanol, both individually and in mixtures with each other. Acetone and methanol were both found to be much more effective extraction solvents than water. Analysis of the extracts revealed the presence of at least six other chemical species besides DNT. Four of these other species were tentatively identified as 2,4-dinitro-benzyl alcohol, 2,4-dinitro-benzaldehyde, 2,4-dinitro-benzoic acid, and 2,4-dinitro-methylbenzoate. The presence of these derivative compounds suggests that some of the DNT undergoes chemical reactions while attached to the carbon surface.

1. INTRODUCTION

Army munitions facilities routinely generate aqueous effluents contaminated with nitrated organics such as 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and 1,3,5-trinitrohexahydro-1,3,5-triazine (RDX). In order to prevent environmental release of such compounds, the effluent streams are treated with granular activated carbon (GAC) prior to discharge. This creates another problem, however, because the activated carbon must be disposed of when it is spent.

The only disposal option currently available for explosive-contaminated carbon is landfilling at an approved hazardous-waste disposal site. This practice is costly and is becoming increasingly unacceptable as public pressure grows to develop alternative technologies for hazardous waste disposal. Regeneration and reuse of the spent carbon is being considered by the Army as one possible method for reducing reliance on land disposal. While the carbon must still ultimately be disposed of or destroyed when it can no longer be regenerated, extending the useful life of the carbon directly reduces the final waste volume.

Various technologies have been considered for regenerating the explosives-laden carbon, including those based on thermal degradation or solvent extraction of the contaminants (1-6). All of these technologies involve the common concerns of minimizing personnel exposure to explosive and toxic hazards while at the same time maximizing the efficiency of the carbon regeneration. A key part of addressing these concerns is the accurate measurement and control of the nitrobody loading on the carbon. When actual carbon analyses are incomplete or unavailable, some basis must still be provided for estimating the magnitude and variability of the contaminant species.

Previous studies of spent munitions carbon have focused on two major contaminants, TNT and RDX (1-6). This study is concerned with the adsorption/desorption behavior of DNT, which is a major nitrobody effluent from TNT manufacturing plants (such as Radford Army Ammunition Plant) and is probably the least studied of the major wastewater contaminants. Two commercial activated carbons (Filtrisorb 300 and Filtrisorb 400) produced by Calgon Corporation were evaluated because they are representative of the majority of the GAC used for munitions wastewater treatment. The primary objectives of this report are:

- to provide basic information needed for the development of chemical analysis procedures for explosive-contaminated carbon,
- to provide a basis for estimating the maximum levels of DNT contamination on spent carbon,
- to provide a basis for estimating the maximum regeneration possible for DNT-contaminated carbon by means of solvent extraction, and
- to provide basic information which could be useful in developing new, more cost effective carbon regeneration processes.

2. EXPERIMENTAL METHODS

Materials

2,4-Dinitrotoluene (Aldrich, 97%) was purified as described earlier (7). Methanol (Fisher, HPLC grade) and acetone (Fisher, certified ACS) were used as-received without further purification. Water was deionized and double distilled. Granular activated carbons (Filtrisorb FS 300, 0.8-10mm, and Filtrisorb FS 400, 0.55-0.75mm) were obtained from Calgon. The FS 300 was used in the as-received size as well as being ground to 90 x 212 microns, while the FS 400 was used only in the as-received size. Both granular carbons were washed several times with distilled water to remove the fines and then dried at 105 deg C for three days.

Adsorption and Desorption Procedures

Adsorption Characterization

The adsorption capacities of the virgin and extracted carbons were measured by batch isotherm tests. In each case, a known weight of carbon was added to a measured weight of aqueous DNT solution (10 to 20 g with 25 to 120 ppm DNT), and the mixture placed in a small glass bottle (approximately 30 ml) with a glass stopper. The glass bottles were then shaken for at least three days (at about 23 deg C) on an Ederbach shaker. After contacting, the samples were centrifuged and the aqueous phase was analyzed by either high-performance liquid chromatography (HPLC) or by ultraviolet spectro-photometer.

Desorption Characterization

Some of the desorption experiments were conducted with carbon loaded in the batch adsorptions. In addition, larger

amounts of DNT-loaded carbon were produced for the desorption experiments by passing concentrated aqueous DNT solutions (at 4 ml/min) through a small vertical glass column packed with carbon (2 to 3 cm high, 0.50 cm diameter). The carbon was held in place with a porous teflon plug and glass wool on the bottom. The spent carbon was then filtered, rinsed with a small amount of water (<1 ml), and dried on filter paper in a ventilated fume hood for at least three days. Typically, the spent carbon prepared in this fashion contained 30 to 40 wt% DNT (approximately 430 to 665 mg DNT/g dry carbon).

Desorption experiments were conducted using column, batch, and Soxhlet procedures. In the column procedure, the spent carbon was packed in the small glass column described above and eluted with 3-5 ml/min of solvent. The solvents used were water, acetone, and methanol. In the batch procedure, 20 to 100 mg of carbon were shaken at room temperature with approximately 10 g of solvent. The shaking times used were seven days for water and ≥ 1 day for acetone and methanol. Higher temperature batch extractions were also carried out by placing the samples in a water bath and stirring them occasionally. In the Soxhlet procedure, approximately 100 mg of carbon was refluxed with approximately 300 ml of solvent at atmospheric pressure for one day. The extracts resulting from the desorption procedures were characterized by HPLC and GC/MS. Acetone extracts of the virgin uncontaminated carbon were run as controls.

Analytical Methods

The concentration of DNT in water was analyzed by either a high-performance liquid chromatograph (HPLC) equipped with a Varian Vari-Chrom UV-VIS detector (reverse-phase column 25 cm long, 4.6 mm i.d., packed with Alltech C18) or by a Perkin-Elmer 559 UV-VIS spectrophotometer. The instruments were calibrated using standard solutions of DNT in water. DNT solutions in acetone and methanol were first diluted with water, and then the organic solvents were evaporated before HPLC or spectrophotometer analysis.

Compounds desorbed from the carbon were characterized by HPLC and gas chromatography/mass spectroscopy (GC/MS). For HPLC, the extracts were diluted with water prior to injection into the instrument. For GC/MS, the extract solutions were filtered, the solvent evaporated, and the residue dried under nitrogen for several hours. The dried residue was then silylated with MSTFA (N-methyl-N-trimethylsilyl-trifluoroacetamide) (Pierce) before injection into the GC/MS. The GC/MS used was a Hewlett-Packard model HP 5995A fitted with a Durabond I narrow-band fused silica column (J. W. Scientific). The column temperature was

programmed from 90 deg C (1-minute hold) to 300 deg C with a 10 deg C/min temperature ramp.

3. RESULTS AND DISCUSSION

Adsorption Isotherms for Virgin and Regenerated Carbon

The adsorption capacities of DNT on FS 300, FS 400, powdered FS 300, and regenerated FS 300 and FS 400 were measured by the batch method and fitted as Freundlich isotherms (8,9). Although the mechanisms are not clearly understood, adsorption of dilute aqueous organics on activated carbon has been found to generally follow the Freundlich equation. Thus the DNT adsorption isotherms can be expressed as follows:

$$X/M = k C_f^{1/n} \quad (1)$$

or

$$\log X/M = \log k + 1/n \log C_f \quad (2)$$

where X/M is the amount of DNT (mg) adsorbed per gram of carbon at equilibrium, X is the amount of DNT (mg) adsorbed by carbon, M is the weight (g) of the carbon, C_f is the concentration (ppm) of the aqueous phase at equilibrium, and k and n are constants for a given adsorption system.

For the DNT concentrations in this study, Eqn. (2) appears to hold true, and log-log plots of X/M vs C_f give straight lines with slope $1/n$ and intercept k at $C_f=1$ ppm. The intercept k is an indication of overall adsorptive capacity. The slope $1/n$ indicates the characteristic energy of adsorption, with smaller values reflecting a lower energy (6,9).

Figures 1 and 2 show the linear least-square fits for each of the two virgin carbons and the corresponding acetone-regenerated carbons, respectively. Figure 3 shows the adsorption isotherm for the powdered virgin FS 300. From the intercept values (that is, X/M at $C_f=1$ ppm), the adsorption capacities of virgin FS 300, virgin FS 400, and virgin powdered FS 300 are approximately 210, 300, and 250 mg DNT/g C, respectively. The corresponding isotherm slopes are 0.171, 0.223, and 0.333, respectively ($n = 5.83, 4.49$, and 3.33). The measured $1/n$ value of 0.333 for powdered FS 300 is roughly in agreement with a reported value of 0.31 for a similar activated carbon (10). Overall, it appears that granular and powdered FS 300 have lower DNT adsorption capacities than FS 400.

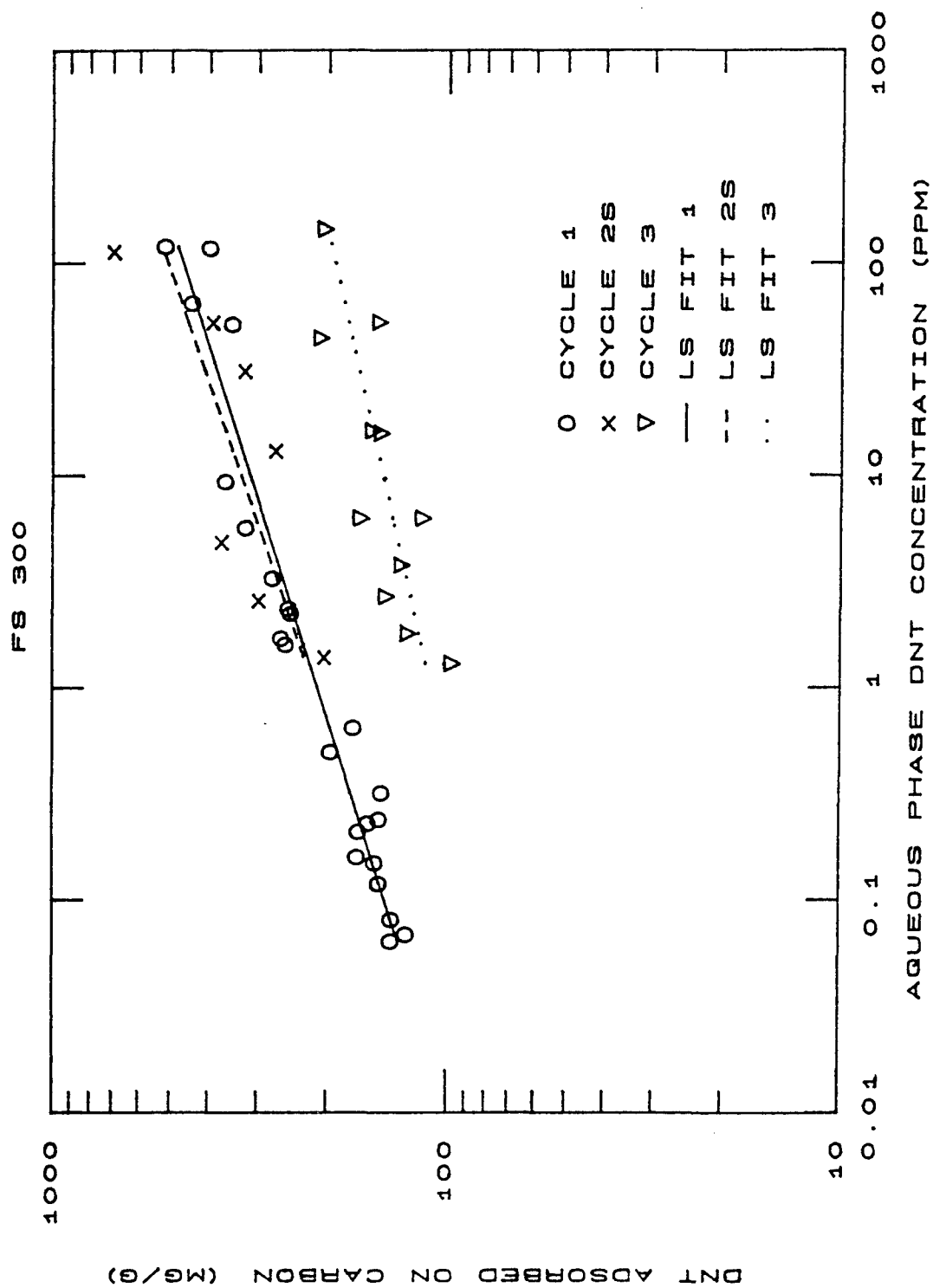


Figure 1. Equilibrium adsorption isotherms for DNT on Calgon FS 300.

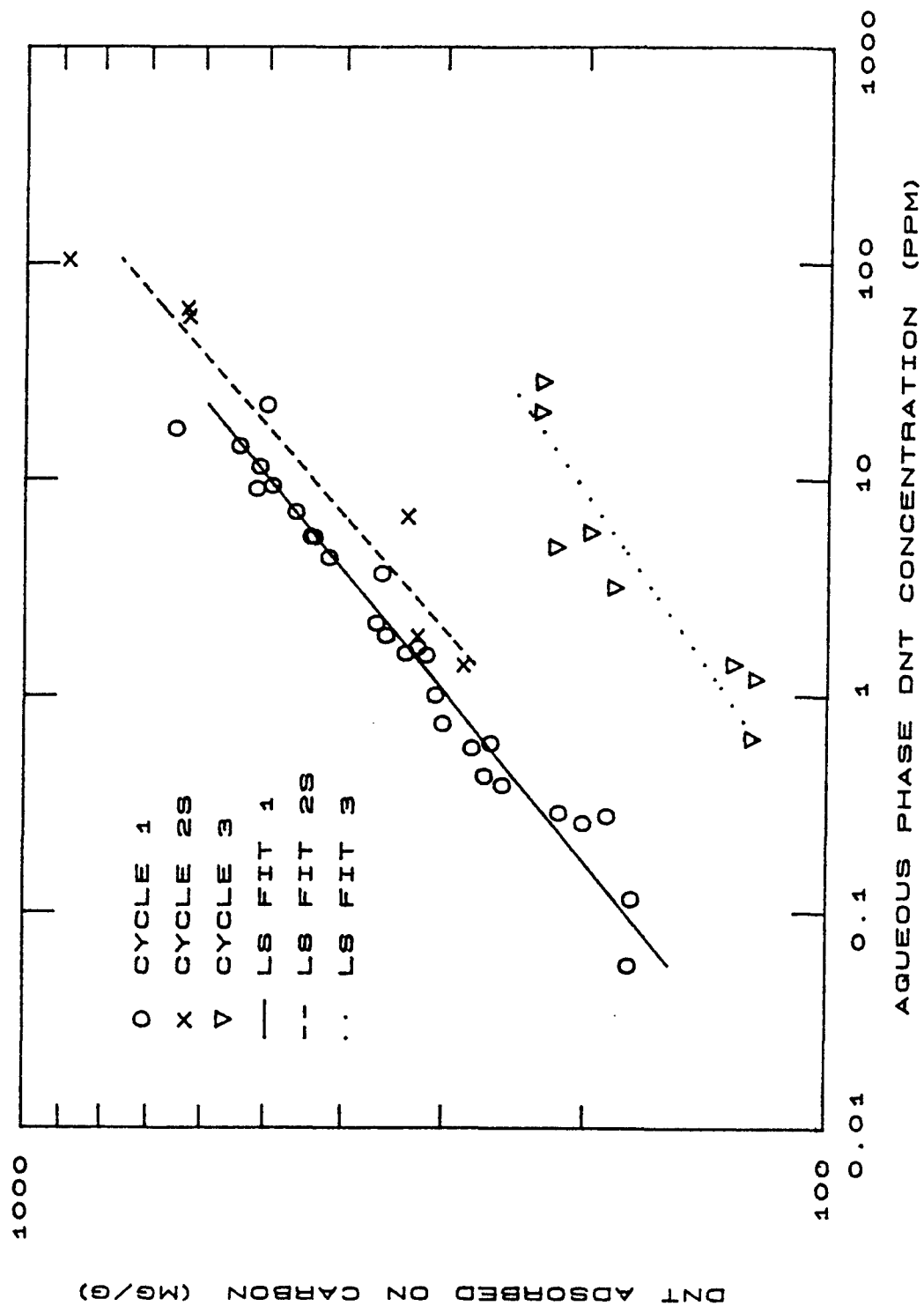


Figure 2. Equilibrium adsorption isotherms for DNT on Calgon FS 400.

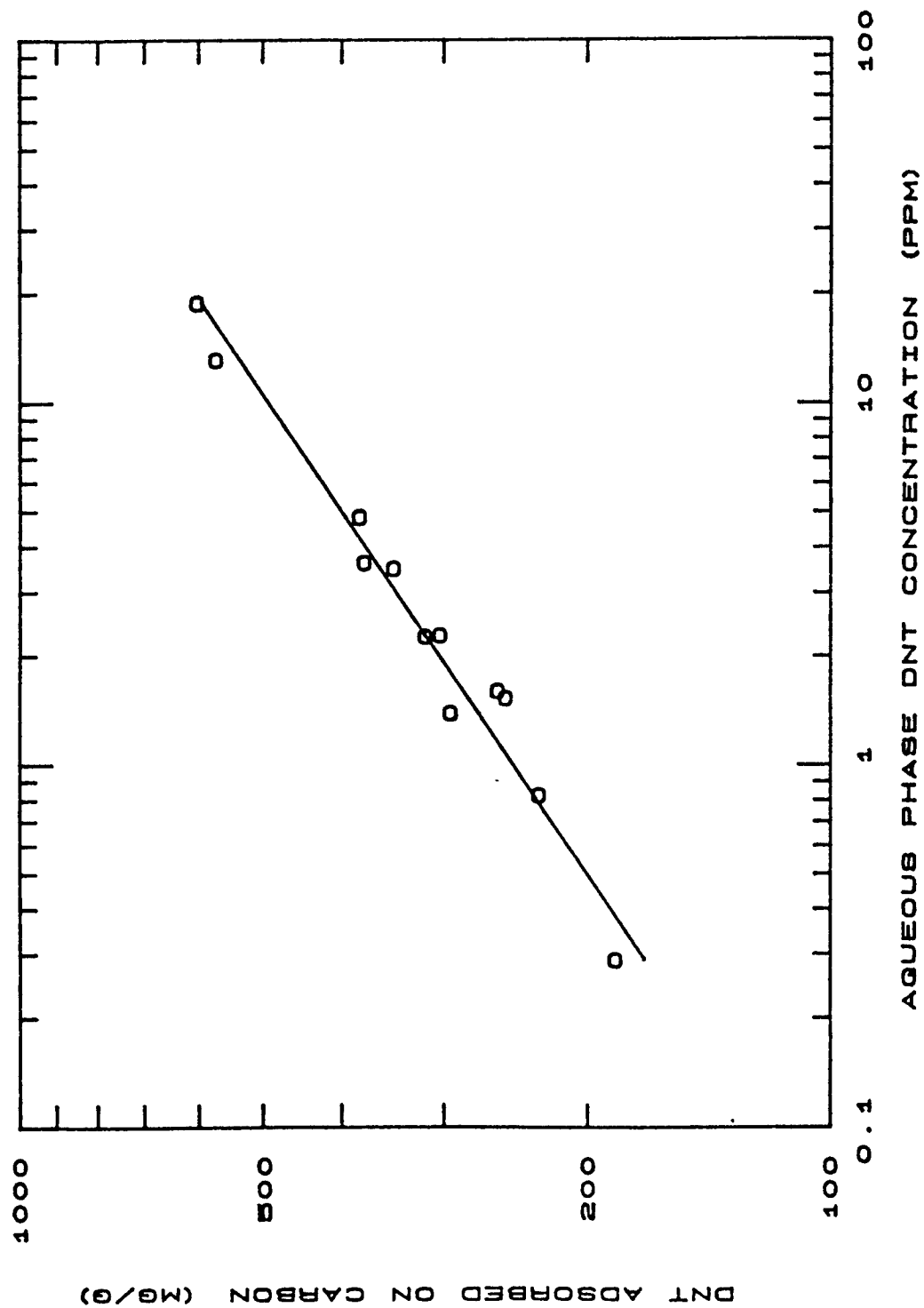


Figure 3. Equilibrium adsorption isotherm for DNT on crushed Calgon FS 300 (90 x 212 microns).

There are two complicating factors in using the above adsorption data to estimate DNT loadings on spent carbon: 1) the DNT levels are likely to vary considerably in actual AAP wastewaters, and 2) when other nitroaromatics are present, the equilibrium DNT loadings can also be less than those reported above due to the competition for adsorption sites. In spite of these complications, however, a reasonable upper limit for the DNT loading on spent carbon can still be estimated. One approach is to make the conservative assumptions that the column input is saturated in DNT and that the DNT loading on the carbon approaches its equilibrium value as the carbon becomes spent. At 25 deg C the saturation concentration of DNT is approximately 250 ppm, yielding equilibrium loadings of 540 and 1030 mg DNT/g C for virgin FS 300 and virgin FS 400, respectively (this translates to about 35% and 51% of the total dry weight).

After DNT adsorption, the spent carbons were regenerated by acetone extraction. Three adsorptions and two desorptions were performed on each carbon (cycle 1: adsorption on virgin carbon; cycle 2: first desorption and second adsorption; cycle 3: second desorption and third adsorption). Desorption was accomplished by the Soxhlet method in cycle 2 and the room temperature batch method in cycle 3. Figures 1 and 2 show that the adsorption capacities of FS 300 and FS 400 after Soxhlet extraction are nearly as great as the virgin carbon, whereas the capacities after batch extraction are drastically decreased.

The relative efficiency of the Soxhlet and batch extraction methods is further demonstrated by the Freundlich isotherms in Figures 4a and b. In this case, two portions of the same spent carbon were regenerated, one portion being extracted by the Soxhlet procedure and one portion being extracted by the batch procedure. The Soxhlet-extracted carbon exhibited at least a 40% better recovery of adsorptive capacity than the batch-extracted carbon.

Desorption with Different Solvents

DNT-loaded FS 300 and FS 400 were extracted with water, acetone, methanol, and their mixtures by column, batch, and Soxhlet procedures separately. Table 1 compares the percentage DNT removal achieved for each solvent system with the Soxhlet method. As expected, both acetone and methanol proved to be better solvents than water.

Figure 5(a) illustrates the effects of solvent/spent carbon weight ratio and temperature on the degree of DNT removal by water using the batch extraction method. Based on this figure, the desorption of DNT in water appears to

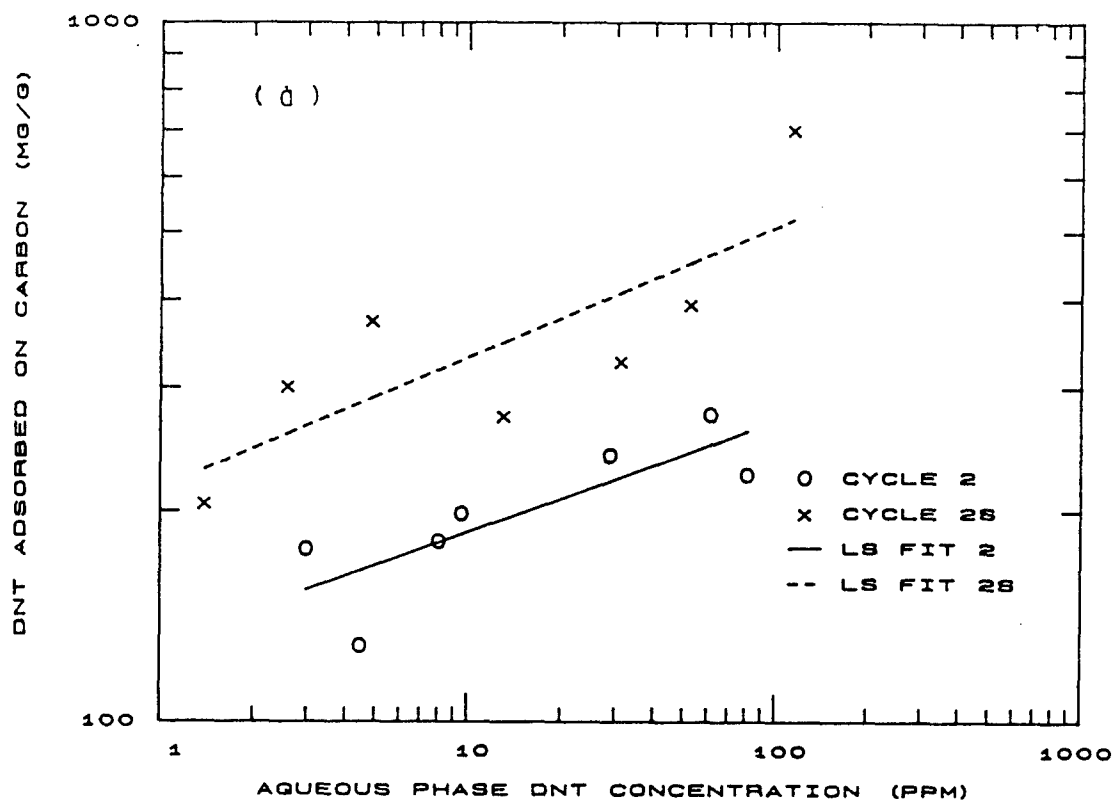


Figure 4a. Comparison of the acetone extraction efficiencies for Calgon FS 300 using simple batch and Soxhlet extraction procedures.

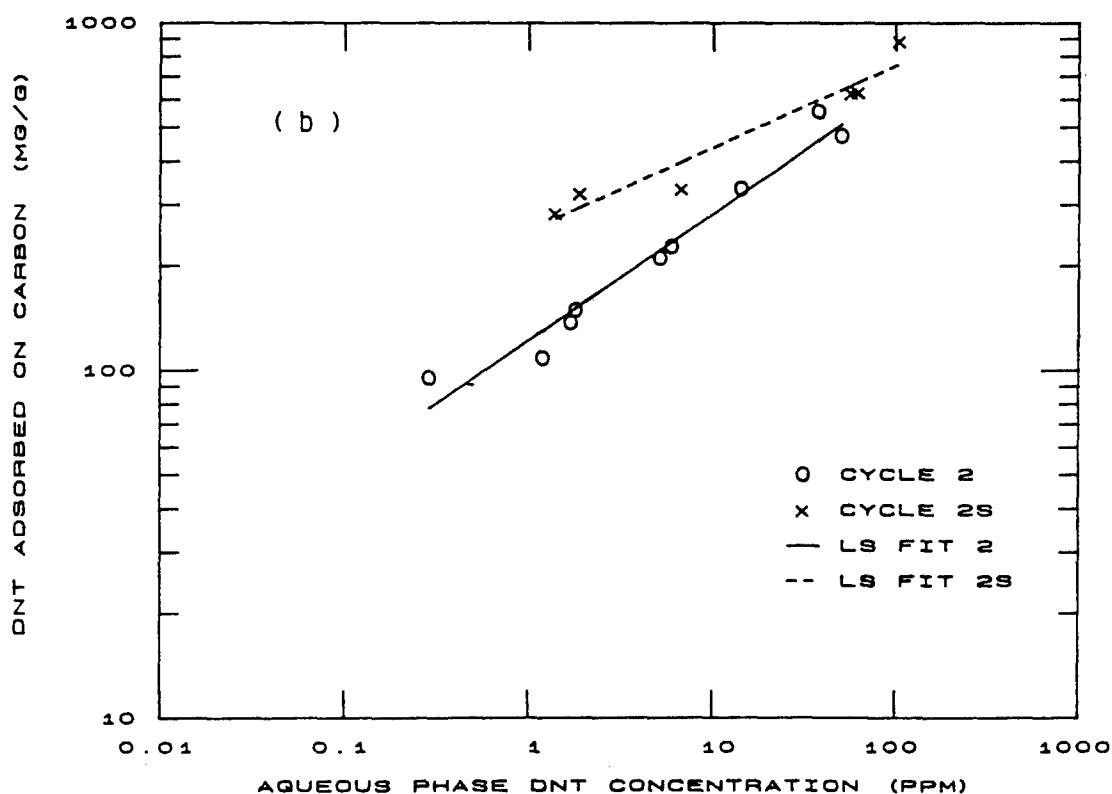


Figure 4b. Comparison of the acetone extraction efficiencies for Calgon FS 400 using simple batch and Soxhlet extraction procedures.

Table 1.
Effectiveness of DNT Extraction by the Soxhlet Method

<u>Solvent</u>	<u>Carbon</u>	<u>% DNT Removed</u>
Water	FS 300	21.2
	FS 400	35.8
Acetone	FS 300	84.1
	FS 400	94.6
Acetone/Water (1:1 by weight)	FS 300	83.3
	FS 400	90.7
Methanol	FS 300	86.9
	FS 400	90.9

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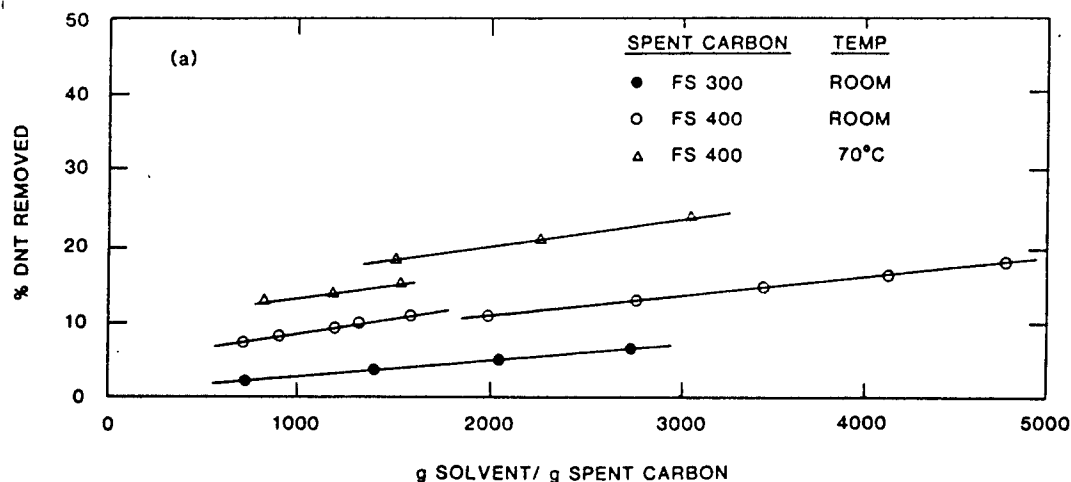


Figure 5a. Effect of the solvent/carbon ratio and temperature on the batch extraction of DNT with water.

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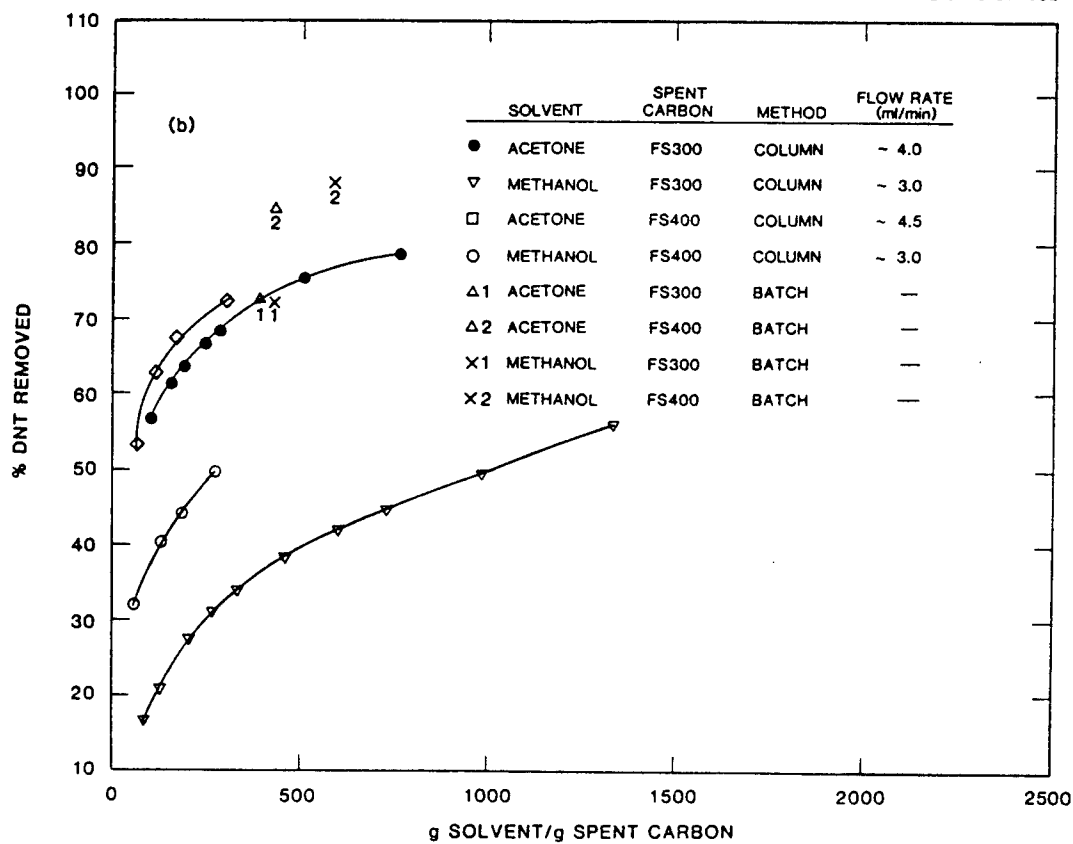


Figure 5b. Effect of the solvent/carbon ratio, temperature, and contacting procedure on extraction of DNT with acetone and methanol.

increase linearly with the water/carbon ratio and also increases significantly as temperature is increased from 23 to 70 deg C. These trends are expected, at least in general, because the DNT carrying capacity of the aqueous phase increases as the water/carbon ratio and temperature increase.

The magnitude of the temperature effect on extractability is supported by Figure 6, which illustrates the rapid increase of DNT solubility in water with temperature. Even with the large temperature effect, however, DNT extraction with water is rather inefficient. At 70 deg C (the melting point of DNT), a water/carbon ratio of 3000 results in only about 25% extraction of the adsorbed DNT from FS400.

Figure 5b illustrates the much greater extraction efficiency of acetone and methanol. Under good contacting conditions, approximately 85% of the DNT can be extracted from FS300 and FS400 at an acetone/carbon ratio of 500. Beyond about 75% removal, the incremental extraction efficiency decreases and 100% removal is approached asymptotically.

The large variation between the different experimental runs in Figure 5 illustrates the importance of contacting efficiency between the carbon and the solvent. Column desorption always involves some "bypassing" of the solvent, especially in short columns similar to the one used here. (Although not done in this case, such bypassing inefficiency can be at least partly compensated by solvent recycle). Some of the differences between the methanol and acetone column extraction efficiencies may have been due to differences in the column voidage and the flow rate. The batch experiments provided more efficient contacting and gave, correspondingly, the highest extraction yields. While the batch extraction efficiencies of both acetone and methanol appear similar, acetone appears to be more efficient for removing the byproduct species. This is discussed more fully in the following section.

Analysis of Desorption Extracts

The HPLC and GC/MS analyses revealed significant differences among the various extracts and the presence of previously unreported chemical byproducts (in contrast to the control extracts of the virgin carbons). Two examples are illustrated in Figures 7 a&b. Figure 7a is an HPLC spectrum for a methanol extract of spent FS 400 (first cycle, column procedure), and 7b is an HPLC spectrum for a subsequent batch acetone extract of the previous methanol-extracted sample. These spectra indicate that most of the DNT was removed by the initial methanol extraction, and also

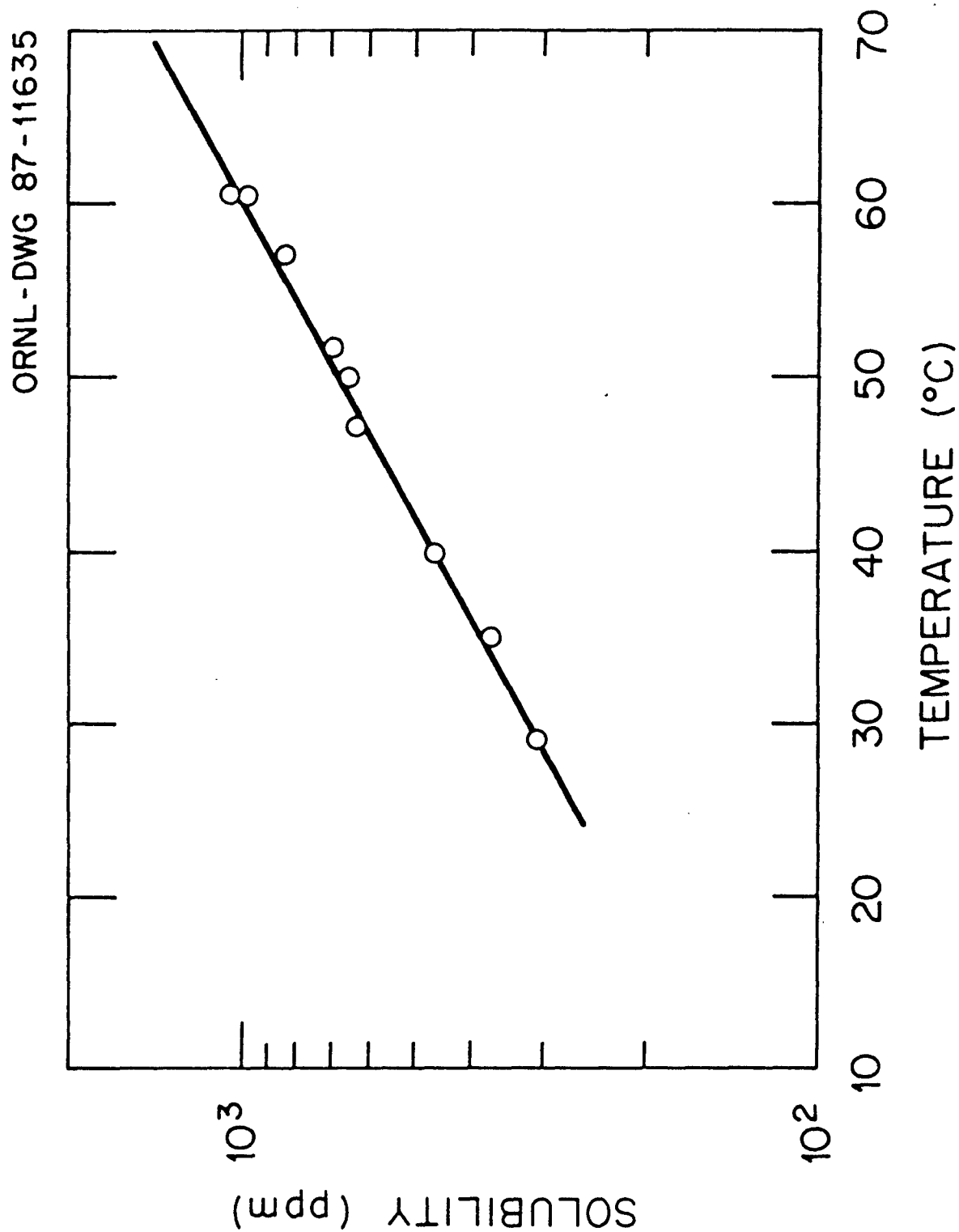


Figure 6. The solubility of DNT in distilled water.

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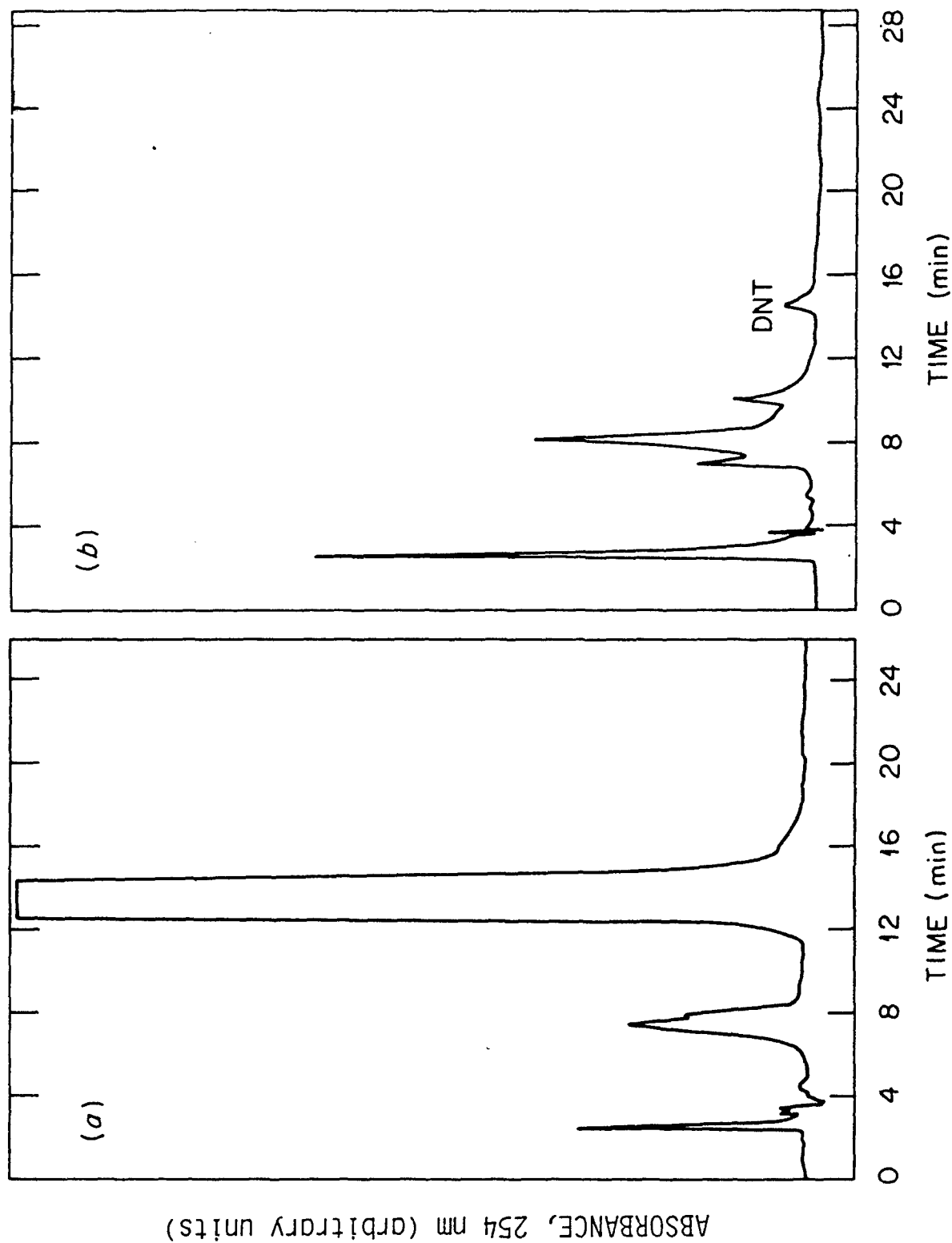


Figure 7. HPLC/UV chromatograms of spent FS 400 extracts: a) methanol, column procedure on freshly prepared spent carbon; b) acetone, batch procedure on carbon previously extracted in part a.

that some of the DNT was converted to other chemical byproducts which were subsequently removed by the acetone.

The variety and relative abundance of byproduct species appearing in the extract appear to depend on the solvent used and the number of adsorption/desorption cycles the carbon experiences. Acetone is the most efficient for byproduct extraction, followed by methanol and then water. In the experiments reported here, there were typically three to six distinct byproducts appearing in the extracts for carbon which had only undergone one adsorption cycle, while there were as many as eight in acetone extracts from second and third cycles. When water was the solvent, the number and abundance of the extracted byproducts increased with temperature.

Figures 8 a, b, and c illustrate HPLC spectra of water, methanol, and acetone extracts, respectively, of DNT-loaded FS 400 (first extraction, batch method). Based on HPLC spectra with pure reference standards, 2,4-dinitrobenzoic acid is a major byproduct appearing in all three extracts. The compound 2,4-dinitrobenzaldehyde also appeared in all three extracts, although its level was rather low in water. Other compounds that could be identified were 2,4-dinitrobenzyl alcohol in the methanol and acetone extracts and 2,4-dinitromethylbenzoate in the acetone extract. The other compounds present have not yet been identified.

Hypothesis for Byproduct Formation

The presence of the chemical byproducts suggests that DNT can undergo chemical reactions after it becomes attached to the carbon surface. The prevalence of partially oxidized DNT derivatives further indicates that one of the major reactions is side-chain (methyl-group) oxidation (7). This is consistent with the observation that activated carbons have large surface areas containing various reactive groups such as carboxyl groups, oxides, and oxygen-containing free radicals (5,11,12).

Because the carbon surface is highly heterogeneous, both physical and chemical adsorption are possible. We speculate that some of the chemically reactive sites serve as catalysis centers, where the DNT can be partially oxidized and then desorbed into the solvent. Highly reactive centers may involve polymerization or direct reaction between the DNT and the carbon substrate, producing compounds which can not be extracted. Further elucidation of the reaction mechanisms may reveal methods for controlling and enhancing DNT oxidation, producing compounds which might be less dangerous and/or more easily removed from the spent carbon.

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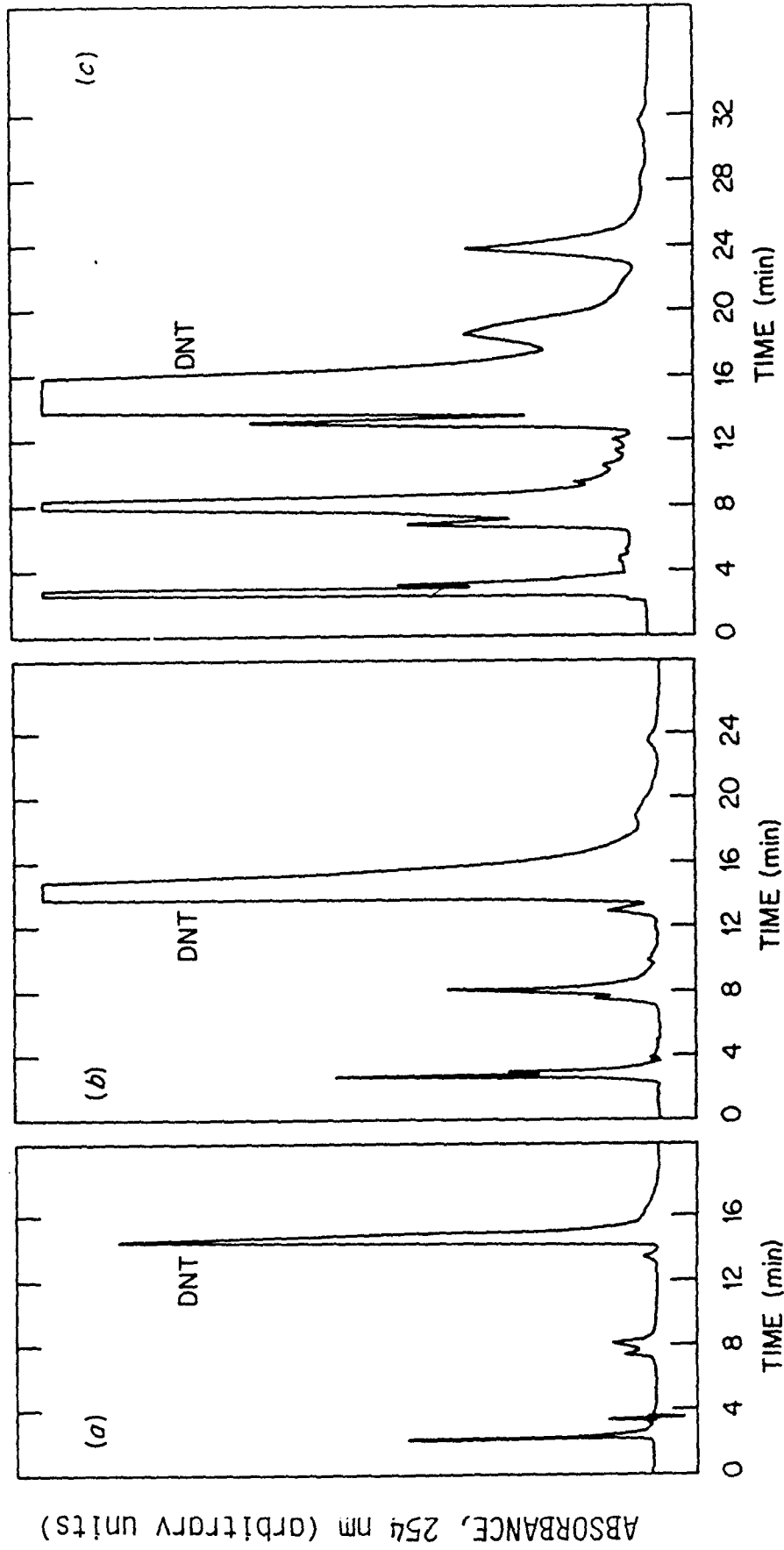


Figure 8. HPLC/UV chromatograms of spent FS 400 extracts: a) water, batch procedure, first extraction; b) methanol, batch procedure, first extraction; c) acetone, batch procedure, first extraction.

4. CONCLUSIONS

- The aqueous DNT adsorption capacities of Calgon FS 300 and FS 400 are different, with FS 400 being generally more adsorptive. Grinding FS 300 increases its adsorptive capacity, but the capacity still remains less than that of FS 400.
- For an aqueous-phase DNT concentration of 250 ppm (saturated at 25 deg C), it is possible to achieve equilibrium DNT loadings on virgin FS 300 and FS 400 as high as 540 and 1030 mg DNT /g of dry carbon, respectively. Such high loadings could have significant impact on handling safety.
- Acetone and methanol are both highly efficient solvents for extracting DNT from activated carbon. Extraction efficiencies of up to 85% can be achieved with a solvent/carbon weight ratio of 500 at room temperature.
- The extraction efficiency of water for DNT on carbon can be increased by raising the water temperature. However, temperatures as high as 70 deg C still result in an extraction efficiency much lower than is possible with acetone or methanol.
- The Soxhlet reflux method is significantly more efficient than room-temperature batch or column methods for removing DNT and its byproducts from carbon.
- Some of the adsorbed DNT is converted to byproduct compounds. The byproducts tentatively identified so far are 2,4-dinitrobenzoic acid, 2,4-dinitrobenzaldehyde, 2,4-dinitrobenzyl alcohol, and 2,4-dinitromethylbenzoate.

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